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Surface Smoothing Mechanism of Amorphous Silicon Thin Films

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An important concern in the deposition of thin hydrogenated amorphous silicon (*a*-Si:H) films is to obtain smooth surfaces. Herein, we combine molecular-dynamics simulations with first-principles density functional theory calculations to elucidate the smoothing mechanism of plasma deposited *a*-Si:H thin films. We show that the deposition precursor may diffuse rapidly on the *a*-Si:H film surface via overcoordinated surface Si atoms and incorporate into the film preferentially in surface valleys, with activation barriers for incorporation dependent on the local surface morphology. Experimental data on smoothing and precursor diffusion are accounted for.

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Thin films of hydrogenated amorphous silicon (*a*-Si:H) are technologically important amorphous semiconductor materials with a broad range of applications in the fabrication of electronic and photovoltaic devices [1,2]. Practical applications are often limited by rough surface morphologies and associated surface and interface coordination defects that reduce carrier lifetimes. Device-quality *a*-Si:H thin films are typically grown by plasma-assisted deposition from silane (SiH₄) containing discharges under conditions where the silyl (SiH₃) radical is the dominant deposition precursor [3]. Based on the exceptionally low surface roughness of *a*-Si:H films grown under these conditions over the temperature (*T*) range 450 K < *T* < 750 K [4,5], a “surface valley-filling” mechanism has been postulated; according to this mechanism, a mobile surface species, generally assumed to be the SiH₃ radical [5], passivates preferentially dangling bonds (DBs) of Si atoms located in surface valleys [4,6]. Experimental data for the roughness evolution of *a*-Si:H films provide only indirect interpretations for the smoothing mechanism [7–11] and yield controversial results for the diffusion barrier of the SiH₃ radical on the *a*-Si:H surface [7,8,12,13]. Moreover, there exists no detailed account of either the role of surface morphology in affecting the incorporation of SiH₃ radicals into the film, or of the preferential locations for growth on the *a*-Si:H surface.

In experimental studies of *a*-Si:H film surface evolution, additional models for surface diffusion, like the solid-on-solid model [8], or assumptions such as that of a weakly adsorbed precursor state [9], or of a self-similar surface morphological evolution [7] typically need to be invoked to connect measured data for the surface topography to kinetic parameters. Reported barriers for precursor diffusion on *a*-Si:H surfaces are dependent on the model employed and vary between 0.2 eV [7] to ~1 eV [8]. In addition, density functional theory (DFT) calculations performed on the hydrogen-terminated crystalline Si(110) surface have been used to propose the existence of a mobile state of the adsorbed SiH₃ radical, in which the radical

diffuses with an energy barrier of 0.4 eV between nearest-neighbor surface Si atoms on this crystalline surface [14]. In phenomenological kinetic models of *a*-Si:H film growth, it is commonly assumed that the diffusing SiH₃ radical incorporates into the *a*-Si:H surface by passivating surface Si DBs [15] and, thus, contributes to growth. Dangling bonds, however, may not be the only viable sites for growth, since their low concentration [16,17] is incompatible with the observed high film growth rates [3]. Therefore, in spite of the above studies, the fundamental mechanisms underlying SiH₃ radical migration, as well as the role of surface morphology in determining Si incorporation into the amorphous film, remain unclear.

In this Letter, we report results of molecular-dynamics (MD) simulations on *a*-Si:H surfaces, used in conjunction with first-principles DFT calculations on the crystalline Si(001)-(2 × 1):H surface, to elucidate the mechanism of surface smoothing of *a*-Si:H thin films. We find that the smoothing mechanism of *a*-Si:H films consists of two steps, namely, the fast diffusion of a deposition precursor on the film surface and, subsequently, the incorporation of the deposition precursor in surface valleys of the *a*-Si:H film. We show that there exists a mobile diffusion state of the SiH₃ radical where the DB of the radical binds to a fourfold coordinated surface Si atom, which, as a result of the radical’s attachment, becomes fivefold coordinated. Furthermore, we find that the Si atom of the SiH₃ radical incorporates preferentially in surface valleys of rough *a*-Si:H films, through an H-transfer-mediated reaction that has a lower activation barrier in surface valleys compared to hills. Our analysis also reveals that the residence time of the growth precursor is longer in surface valleys than on surface hills. The increased residence times of the growth precursor, combined with the preferential incorporation into surface valleys of the *a*-Si:H film, lead to an effective smoothing mechanism.

The *a*-Si:H films used in this study were prepared over the range 475 K ≤ *T* ≤ 800 K by MD as described in Refs. [18,19]. In the MD simulations, the interatomic

interactions were described by an extended Tersoff potential for Si to include Si-H, H-H, and the corresponding three-body interactions [20]. MD simulations based on this potential have reproduced successfully structural properties and surface chemistry of plasma deposited *a*-Si:H films [19,21]. We studied the diffusion mechanism of the SiH₃ radical by generating 24 MD trajectories of 120 ps duration at each *T* on smooth *a*-Si:H films. The diffusion coefficient (*D*) and activation barrier (*E_a*) were obtained through monitoring of the radical's mean squared displacement (MSD) and an Arrhenius plot of *D* vs *T*, respectively; multiple origins were chosen when evaluating ensemble averages of the MSD [22]. Si incorporation processes from the SiH₃ radical precursor were studied on an ensemble of 154 MD trajectories of 80–400 ps duration on rough *a*-Si:H films deposited at 500 K and 773 K. DFT calculations were implemented within the generalized gradient approximation and employed slab supercells, plane-wave basis sets [23], and ultrasoft pseudopotentials [24]. Diffusion pathways were constructed by employing the nudged elastic band method that included a climbing image [25] to obtain saddle-point configurations and activation barriers. Our DFT calculational methodology has been described in detail in Ref. [26].

Analysis of the evolution of the ensemble-averaged MSD yields an *E_a* for SiH₃ radical diffusion on the smooth *a*-Si:H surface of 0.16 ± 0.01 eV, with a prefactor $D_0 = (1.82 \pm 0.07) \times 10^{-3}$ cm²/sec. The analysis also reveals that the surface Si atom to which the SiH₃ radical is bonded is typically fivefold coordinated and, consequently, the radical-surface interaction is weakened. During migration, the SiH₃ radical breaks easily its weak Si-Si bond with the surface Si atom and hops to an adjacent Si atom that again becomes fivefold coordinated as a result of its bonding with the radical's Si; in the transition state, the radical is bonded to both of the surface Si atoms that it hops between. The overcoordination of surface Si atoms is due to the diffusing radical and this "overcoordinated state" accompanies the radical on its pathway. The radical continues its migration on the *a*-Si:H surface in this manner until it incorporates into the film. Therefore, the low barrier for diffusion is due to the weak adsorption of the SiH₃ radical onto the *a*-Si:H surface and its migration predominantly through overcoordination defects.

We have validated the low radical diffusion barrier on the *a*-Si:H surface by performing first-principles DFT calculations of SiH₃ migration on the ordered Si(001)-(2 × 1):H surface for radical migration through overcoordinated sites. We have found that the SiH₃ radical adsorbed on a Si atom of a surface Si-Si dimer corresponds to an equilibrium configuration, which is shown in Fig. 1(a). In this configuration, the dimer Si atom is fivefold coordinated. An analysis of the corresponding local density of states shows that the originally dangling electron of the SiH₃ radical is distributed at this adsorbed state primarily among six atoms: the dimer Si atom to which the radical is bonded and its five neighbors. A specific hopping process is exam-

FIG. 1 (color online). (a) Top view of the ordered Si(001)-(2 × 1):H surface with an SiH₃ radical adsorbed on a Si atom of a surface Si-Si dimer. The arrow outlines an SiH₃ hopping event from a top-layer Si atom to a nearest-neighbor 2nd-layer Si atom. (b) Valence electron density distribution in the plane of the two surface Si atoms the radical is hopping between (Si1 and Si2) and the radical's Si atom (Si3) at the saddle-point configuration of the radical's hopping path. (c) Corresponding total energy, *E*, as a function of a migration coordinate, ξ .

ined, where the radical hops from the dimer Si atom to an adjacent Si atom in the 2nd layer, as shown in Fig. 1(a). The dimer Si and the 2nd-layer Si atom also are bonded to each other and they both share part of the wave function of the localized surface state, which is induced by the bonding of the radical. Throughout this hopping path, there is considerable overlap between the *sp*³ orbital of the Si atom of the SiH₃ radical and the wave function of the surface state induced by the radical; i.e., the radical always stays bonded to the surface. This is demonstrated by the high valence electron density between the radical's Si atom and the two Si atoms of the surface between which the radical is hopping, even in the saddle-point configuration, as shown in Fig. 1(b). As a result, part of the radical's dangling electron remains constantly localized on the surface and the localized surface state follows the diffusing radical along its pathway, as long as it is hopping between nearest-neighbor overcoordinated Si atoms on the surface. For this radical hopping event, the DFT analysis yields an activation barrier of 0.18 eV (or 0.25 eV for hopping in the reverse direction), as shown in Fig. 1(c). We conclude that the *E_a* calculated on the *a*-Si:H surface (0.16 eV) is in good agreement with the DFT result. It is important to note that, for this radical hopping event on a crystalline Si surface, the local atomic structure in the vicinity of the SiH₃ radical is identical to that observed on the *a*-Si:H surface during SiH₃ radical migration: this establishes a strong link between the MD-based diffusion study on the *a*-Si:H surface

and the quantitatively accurate DFT calculation of radical hopping on the ordered Si surface.

In addition to elucidating the SiH_3 surface diffusion mechanism, our MD trajectories for radical migration on surfaces of rough a -Si:H films reveals that the diffusing SiH_3 radical is incorporated into the rough a -Si:H film preferentially in surface valleys. The incorporation reaction is accompanied by the transfer of an H atom to a nearby surface Si atom so that the radical can form a second Si-Si bond with the surface. Statistical analysis of the MD trajectories on rough a -Si:H films reveals that H transfer leading to Si incorporation occurs preferentially in valleys in 72% of the cases examined. Also, H transfer to dangling bonds was observed to occur in less than 7% of the trajectories analyzed. Therefore, we conclude that H-transfer reactions do not require the presence of DBs and lead to valley filling even when the DB density is low or DBs are not present in surface valleys. Instead, the Si atom to which the H atom is transferred is typically fourfold coordinated prior to H transfer and becomes fivefold coordinated after H transfer from the radical to the surface.

The preferential incorporation of SiH_3 radicals into surface valleys can be explained in terms of (i) an increased residence time of the diffusing radical in valleys as opposed to hills and (ii) lower activation barriers for H-transfer-mediated Si incorporation in surface valleys. The diffusing radical migrates rapidly from surface hills to valleys, while it remains localized in surface valleys. There is a strong driving force for the radical to migrate from surface hills to valleys due to the surface Si-Si bond strain distribution as determined by the surface topography [27]. Once the radical reaches the valley, it remains localized in the valley, due to the absence of any strong strain-induced driving force to diffuse out of the valley. This increased residence time leads to a better sampling by the radical of reactive surface sites in the valley regions, which causes the H-transfer-mediated Si incorporation reaction to occur preferentially in valleys.

Moreover, detailed energetic analysis of numerous H-transfer reactions yielded an activation barrier for H-transfer-mediated Si incorporation, $E_{a,H}$, that is dependent primarily on the interatomic distance, $d_{\text{Si-Si}}$, between the Si atom of the radical and the surface Si atom to which the H is transferred, prior to H transfer. Figure 2 shows the dependence of $E_{a,H}$ on $d_{\text{Si-Si}}$. The barrier is high when $d_{\text{Si-Si}} < 2.65$ Å, as the Si-Si bond needs to be strained during H transfer from one Si atom to another, or when $d_{\text{Si-Si}} > 3.4$ Å, where the two Si atoms are far apart and the Si-H bond is very strained in the transition state. Therefore, there exists a window, $2.7 \text{ Å} < d_{\text{Si-Si}} < 3.2 \text{ Å}$, that corresponds to low $E_{a,H}$ (< 0.4 eV). In this window, the Si-Si bond is either already strained enough so that H transfer from one Si to another does not require further straining of the bonds, or if there is no bond between the two Si atoms, the Si atoms are still not too far apart to inhibit H transfer. The $d_{\text{Si-Si}}$ distributions for all H-transfer

FIG. 2. Dependence of the activation energy barrier, $E_{a,H}$, for H transfer and subsequent Si incorporation into the a -Si:H surface on the distance, $d_{\text{Si-Si}}$, between the Si atom of the radical and the surface Si atom to which the H is transferred.

events in the valleys and hills are plotted in Fig. 3. Figure 3 reveals that the local environment in valleys is more advantageous for H-transfer reactions because more Si-Si distances fall in the range where the barrier for H transfer is low. The mean interatomic distance in the valleys is lower due to the local surface topology in the valley: surface valleys are concave, while surface hills are convex. This difference in surface curvature induces opposite types of Si-Si bond strain, namely, tensile in hills and compressive in valleys, which affect accordingly (through activation strain) the corresponding activation barriers for reaction. This qualitative explanation is supported by the statistical (quantitative) data of Fig. 3, which, in conjunction with Fig. 2, ensures that the Si incorporation probability is higher in surface valleys than on hills.

Interpretation of experimental data.—Activation barriers $E_a \sim 0.15$ – 0.30 eV have been reported for SiH_3 dif-

FIG. 3 (color online). Distribution of the interatomic distance, $d_{\text{Si-Si}}$, between the Si atom of the radical and the surface Si atom to which the H is transferred, in the surface valleys (blue/gray curve) and on the surface hills (black curve), as observed in the MD simulations over all H-transfer events occurring in the valleys and on the hills.

fusion on smooth *a*-Si:H films through indirect approaches combining experimental measurements with models that assumed certain kinetics for the underlying mechanisms [7,12,13]. For example, Bray and Parsons reported an E_a of 0.20 eV [7] using time-dependent surface topography and dynamic scaling models for *a*-Si:H, while Maeda and co-workers assumed a simplified set of reactions to explain the H concentration in *a*-Si:H films produced by rf glow discharges of SiH₄ and calculated an E_a of 0.30 eV [13]. Our MD simulations represent the first direct calculation of the activation barrier for SiH₃ diffusion on *a*-Si:H surfaces and the calculated value of 0.16 eV is consistent with the above indirect experimental results.

The T dependence of the surface roughening evolution of *a*-Si:H films has been analyzed in several experiments, under conditions where the dominant deposition precursor is the SiH₃ radical [7–11]. Smets and co-workers studied the scaling behavior of the growth surface morphology of *a*-Si:H films and derived an activation energy barrier of ~ 1.0 eV for the smoothening mechanism [8]. However, Kondo and co-workers performed an *ex situ* study of *a*-Si:H surface morphology over the range $50^\circ\text{C} < T < 450^\circ\text{C}$, and indicated a weakly activated smoothening process [10], in agreement with the results of Ref. [7]. Our studies indicate that surface smoothening is limited by Si incorporation in surface valleys with typical activation barriers of 0.3–0.4 eV, which is consistent with the kinetics of the smoothening process reported in Refs. [7,10]. Nevertheless, we expect the activation barrier for H transfer to increase substantially for $d_{\text{Si-Si}} < 2.7$ Å or $d_{\text{Si-Si}} > 3.2$ Å, which could account for the smoothening barriers on the order of 1 eV; in such cases, finer-scale experimental structural characterization would be required for direct comparisons with the experimental findings of Smets and co-workers [8]. We point out that the smoothening mechanism described in this Letter depends only on the local surface morphology and is independent of the thickness of the *a*-Si:H films. Furthermore, we do not expect DB diffusion from hills to valleys to control the surface smoothening mechanism, as proposed in some experimental studies [8,11]. The diffusion of DBs from hills to valleys occurs only when H atoms that are bonded to fourfold coordinated Si atoms diffuse from valleys to hills. The barrier for an H atom to break away from a DB in *a*-Si:H is in excess of 2.5 eV [28] and would lead to DB diffusion over time scales that are much longer than the SiH₃ radical diffusion and Si incorporation time scales observed in our MD simulations.

In summary, we have shown that the surface smoothening mechanism of *a*-Si:H films is a result of the rapid diffusion on the film surface of the deposition precursor and its subsequent incorporation in surface valleys of the *a*-Si:H film. The deposition precursor incorporates preferentially in surface valleys after it transfers an H atom and forms two Si-Si backbonds with the film, even in the absence of surface Si dangling bonds. This surface smoothening mechanism is consistent with both the experimental

a-Si:H film surface roughness evolution data and the observed low surface DB coverage.

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